Citation 3

Application No. Hei-166306

Application Date: June 11, 1993

Publication (KOKAI) No. Hei 6-345839

Publication Date: December 20, 1994

Title of Invention:

Process for producing isocyanate prepolymers and two-pack urethane compositions

Applicant: Taoka Chemical Industry Co.

[Title of Invention]

Process for producing isocyanate prepolymers and two-pack urethane compositions

[Claims]

1. A process for producing an isocyanate prepolymer by reacting 1 mole of a polyalkylene glycol having an average molecular weight of 500 ~ 3000 with 0.1 ~ 0.6 moles of a trifunctional or higher polyhydroxy compound and 1.2 ~ 4.0 moles of an alicyclic polyisocyanate.

2. The process according to claim 1, wherein the isocyanate prepolymer has an average molecular weight of 10,000 ~ 20,000.

3. A two-pack urethane composition comprising an active agent based on a polyisocyanate component and a curing agent, the

active agent component being an isocyanate prepolymer having an average molecular weight of 10,000 ~ 20,000 which is obtained by reacting 1 mole of a polyalkylene glycol having an average molecular weight of 500 ~ 3000 with 0.1 ~ 0.6 moles of a trifunctional or higher polyhydroxy compound and 1.2 ~ 4.0 moles of an alicyclic polyisocyanate, the curing agent component being based on an aromatic amine having a primary and/or a secondary amino group.

[0001]

[Detailed Description of the Invention]

[Industrial Field of Application]

The present invention relates to an improvement of spray coatable two-pack urethane compositions that cure at ordinary temperature to provide coats having high wear resistance.

[0002]

[Prior Art]

Polyisocyanate-based urethane compositions are easy to apply and, after curing, provide highly airtight and waterproof soft elastomers; in addition, they are highly durable and, hence, are extensively used as coatings, joint fillers, adhesives, etc. in civil engineering, construction, machines, marine structures, vehicles and other applications. However, when urethane compositions using polyols as the curing agent harden, there occurs a reaction with the water on the substrate surface and in the air to generate CO_2, producing

cracks at the interface with the substrate and the desired sealing effect is not assured. As another problem, foams occur in the surface layer to cause very unseemly blisters. In order to solve these problems, composition systems have been proposed that comprise an active agent based on isocyanates having low reactivity with water and an aliphatic polyamine based curing agent.

[0003]

[Problems to be Solved by the Invention]

However, the proposed compositions have a very short pot life, so they can be mixed in only small amounts to present a problem, particularly in spray coating. The hardened coats of polyurethane compositions using polyamines as a curing agent generally have high wear resistance but, on the other hand, they are not capable of withstanding prolonged use. A particular problem occurs if they are used at sites that require high wear resistance. The present invention has been accomplished under these circumstances and has as an object providing two-pack urethane compositions that present a long pot life after mixing the active agent component with the curing agent component, that can be sprayed efficiently and that harden in a short time without foaming, thus producing coats having excellent rubber properties, high wear resistance and good aesthetic appeal. The present inventors found that all the problems mentioned above could be solved

simultaneously by using an isocyanate prepolymer of a specified composition and the present invention has been accomplished on the basis of this finding.

[0004]

[Means for Solving the Problems]

The present invention relates to a process for producing an isocyanate prepolymer having an average molecular weight of 10,000 ~ 20,000 by reacting 1 mole of a polyalkylene glycol having an average molecular weight of 500 ~ 3000 with 0.1 ~ 0.6 moles of a trifunctional or higher polyhydroxy compound and 1.2 ~ 4.0 moles of an alicyclic polyisocyanate. The invention also relates to a two-pack urethane composition comprising an active agent based on a polyisocyanate component and a curing agent, the active agent component being an isocyanate prepolymer having an average molecular weight of 10,000 ~ 20,000 which is obtained by reacting 1 mole of a polyalkylene glycol having an average molecular weight of 500 ~ 3000 with 0.1 ~ 0.6 moles of a trifunctional or higher polyhydroxy compound and 1.2 ~ 4.0 moles of an alicyclic polyisocyanate, the curing agent component being based on an aromatic amine having a primary and/or a secondary amino group.

[0005]

The invention is described below in greater detail. To begin with, the process for producing the isocyanate

prepolymer is described. The isocyanate prepolymer of the invention is obtained by reacting a polyalkylene glycol, a polyhydroxy compound and an alicyclic polyisocyanate in an organic solvent, usually in the presence of a catalyst. The polyalkylene glycol to be used in the invention must have an average molecular weight of 500 ~ 3000. If the average molecular weight of the polyalkylene glycol is less than 500, the produced isocyanate prepolymer has such a small molecular weight that the hardened coat will not have adequate wear resistance. If the average molecular weight of the polyalkylene glycol exceeds 3000, the hardened coat will not adhere strongly to the substrate and, in addition, it does not have adequate wear resistance.

[0006]

Polyalkylene glycols that are preferably used in the invention include polyethylene glycol (hereunder abbreviated as PEG and on the following pages, the abbreviations of several compound names are parenthesized), polypropylene glycol (PPG), polytetramethylene ether glycol (PTMG), polyester diol (PED) and polycaprolactone diol (PCD). Polyhydroxy compounds that are preferably used in the invention are trifunctional and higher polyhydroxy compounds and specific examples include glycerin (G), 1,2,3-butanetriol, pentanetriol, diglycerin, trimethylolpropane (TMP) and tetramethylolpropane (TEMP). Alicyclic polyisocyanates that

can be used in the invention include dicyclohexylmethane diisocyanate (HMDI), diisopropylidene bis(4-cyclohexylisocyanate) (IPC), cyclohexyl diisocyanate (CHPI) and isophorone diisocyanate (IPDI).

[0007]

Any organic solvents may be used to produce the isocyanate prepolymer of the invention as long as they do not react with the aforementioned isocyanate and amine but are highly miscible with them. Specific examples include acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), cyclohexanone, tetrahydrofuran and dichloromethane; two or more of these solvents may be mixed without any problem.

[0008]

Catalysts are preferably used in the production of the isocyanate prepolymer of the invention and catalysts that can be used include known organometallic catalysts and/amine catalysts, etc. Exemplary organometallic catalysts include dibutyltin dilaurate, lead octylate, bismuth octoate, etc. and these can be used either alone or in admixture. Exemplary amine catalysts include triethylamine, N,N,N',N'-tetramethylhexamethylenediamine, N-ethylmorpholine, 1,8-diazobicyclo(5,4,0)undecene-7 (DBU), etc. These catalysts are preferably used in amounts of about 0.001 ~ 5 wt% of the total amount of the starting materials used.

[0009]

The thus produced isocyanate prepolymer is used as an active agent component in a two-pack urethane composition in combination with an aromatic amine having a primary or secondary amino group which is used as a curing agent component.

[0010]

Aromatic amines having a primary or secondary amino group that can be used as a curing agent in the invention include: 3,3'-dimethoxy-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 3,3'-dichloro-4,4'-diaminodiphenylmethane, 2,2',3,3'-tetrachloro-4,4'-diaminodiphenylmethane, trimethylene-bis(4-aminobenzoate), polytetramethylene oxide-di-p-aminobenzoate, 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane, 4,4'-diaminodiphenylmethane, 1,1-bis(4-amino-3-methylphenyl)cyclohexane, 1,1-bis(4-aminophenyl)cyclohexane, 4,4'-methylenebis(methylanthranylate), 3,3'-dimethyl-4,4'-diaminobiphenyl-6,6'-disulfonic acid, 4-chloro-3,5-diaminobenzoic acid isobutyl ester, 2,2'-dichloro-4,4'-diamino-5,5'-dimethoxybiphenyl, 2,2',5,5'-tetrachloro-4,4'-diaminobiphenyl, 2,2'-dimethyl-4,4'-diaminobiphenyl, 4,4'-diamino-diphenyl ether, 3,4'-diamino-diphenyl ether, 4,4'-diamino-diphenylsulfone, 1,2-bis[4-(2-aminophenylthio)ethane], 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, etc.

[0011]

The urethane composition of the invention may contain other additives and auxiliary agents, as exemplified by plasticizer, flame retardant, solvent, filler, stabilizer and colorants. Exemplary plasticizers include dioctyl phthalate (DOP), dibutyl phthalate (DBP), dioctyl adipate (DOA), tricresyl phosphate and chlorinated paraffin. Exemplary flame retardants include phosphate esters such as tris-(β-chloropropyl)phosphate (Firol PCF, product of Akzo Japan), tris-dichloropropyl phosphate (CRP, product of Daihachi Chemical) and tris-chloroethyl phosphate (CLP, product of Daihachi Chemical), and reactive bromine compounds such as dibromoneopentyl glycol and tribromoneopentyl alcohol. The plastizer, flame retardant and other additives are each preferably used in amounts of about 5 ~ 30 wt% of the active and curing agents.

[0012]

Exemplary solvents include dichloromethane, acetone, MEK, MIBK, cyclohexane and tetrahydrofuran. Exemplary fillers include calcium carbonate, talc and aluminum hydroxide. Exemplary stabilizers include the following: position hindered phenols such as those available under the trade names Irganox #1010 and #1076 (products of Ciba-Geigy) and Yoshinox BHT, BB and GSY-930 (products of Yoshitomi Pharmaceutical); benzotriazoles such as Tinuvin P, #327 and # 328 (products of

Ciba-Geigy); benzophenes such as Tomisoap #800 (product of Yoshitomi Pharmaceutical); and position hindered amines such as Sanol LS-770 and #744, as well as Tinuvin #144 (products of Ciba-Geigy). Exemplary colorants include inorganic pigments such as red oxide, chromium oxide and lead oxide, or organics such as phthalocyanine or azo based compounds, which are mixed and kneaded with plasticizers at a weight ratio of about 1:1, as well as dyes.

[0013]

[Advantages of the Invention]

A urethane composition containing as the active agent the isocyanate prepolymer obtained by the invention features a long pot life after the active agent component is mixed with the curing agent component and it can be sprayed efficiently, hardens in a short time without foaming, and the hardened coating has outstanding rubber properties, high wear resistance and good aesthetic appeal.

[0014]

[Examples]

The invention is described in even greater detail by referring to examples for the synthesis of the active agent and the curing agent, as well as working examples of the invention.

Active agent synthesis 1

A 1-L four-necked flask equipped with a nitrogen purged stirrer, a condenser and a dropping funnel was charged with 160 g (0.16 moles; molar ratio, 1.0) of polytetramethylene ether glycol (product of Hodogaya Chemical; trade name, PTG-1000; average molecular weight, 1000), 92.2 g (0.35 moles; molar ratio, 2.2) of dicyclohexylmethane diisocyanate (product of Sumitomo-Bayer, Desmodur W), 3.8 g (0.04 moles; molar ratio, 0.03) of glycerin (product of Hayashi Pure Chemical) and 80 g of MEK and thereafter 0.16 g of a toluene solution of 10% dibutyltin dilaurate (product of Hayashi Pure Chemical) was added dropwise to the stirred mixture at 50~60 °C over 30 minutes. After reaction was performed for an additional 3 hours at the same temperature, measurement was done by gel permeation chromatography (GPC), showing that the reaction product had an average molecular weight of 14,000 and that 5% of HMDI remained unreacted. The reaction was then quenched. An additional amount (60 g) of MEK was added and mixed, yielding 390 g of an active agent A-1 with an isocyanate content of 5.2% that had a viscosity of 54 P (poise) at 20 °C.

[0015]

<u>Active agent syntheses 2~17</u>

Using the polyisocyanates, polyalkylene glycols, polyhydroxy compounds, catalysts and solvents listed in Tables 1-a and 1-b, the procedure of Synthesis 1 was repeated to

produce isocyanate prepolymers (active agents A-2 ~ A-17) having the properties (average molecualr weight, viscosity and isocyanate content) described in Tables 2-a and 2-b.

[0016]

[Table 1-a]

Table 1-a

Active agent No.	Polyisocyanate		Polyalkylene glycol		Polyhydroxy compound		Catalyst	Organic solvent
	Name	Charged molar ratio	Name	Charged molar ratio	Name	Charged molar ratio		
1	HMD I	2.2	PTMG-1000	1.0	TMP	0.3	DBU	Dichloro methane
2	HMD I	2.2	PTMG-1000	1.0	TMP	0.3	DBSnL	Dichloro methane
3	HMD I	2.2	PTMG-1000	1.0	TMP	0.6	DBSnL	Dichloro methane
4	HMD I	2.2	PTMG-1000	1.0	TMP	0.1	DBSnL	Dichloro methane
5	HMD I	4.0	PTMG-1000	1.0	TMP	0.1	DBSnL	Dichloro methane
6	HMD I	1.2	PTMG-1000	1.0	TMP	0.1	DBSnL	Dichloro methane
7	HMD I	2.0	PTMG-1000	1.0	TMP	0.1	DBU	Dichloro methane
8	HMD I	2.0	PTMG-1000	1.0	TMP	0.1	DBSnL	Dichloro methane
9	HMD I	2.0	PTMG-1000	1.0	TMP	0.1	DBSnL	Dichloro methane

[0017]

[Table 1-b]

Table 1-b

Active agent No.	Polyisocyanate		Polyalkylene glycol		Polyhydroxy compound		Catalyst	Organic solvent
	Name	Charged molar ratio	Name	Charged molar ratio	Name	Charged molar ratio		
10	HMD I	2.2	PEG-600	1.0	G	0.3	DBSnL	MEK
11	IPC	2.2	PTMG-1000	1.0	TMP	0.3	DBSnL	Dichloro methane
12	IPDI	2.2	PTMG-1000	1.0	TMP	0.3	DBSnL	Dichloro methane
13	HMD I	2.2	PTMG-1000	1.0	-	-	DBSnL	Dichloro methane
14	TMXD I	2.2	PTMG-1000	1.0	G	0.3	DBSnL	Dichloro methane
15	MD I	2.2	PEG-600	1.0	TMP	0.3	DBSnL	Dichloro methane
16	HMD 1	2.2	PTMG-1000	1.0	TMP	0.8	DBSnL	Dichloro methane
17	HMD 1	2.2	PTMG-1000	1.0	TMP	0.05	DBSnL	Dichloro methane

TMXDI : tetramethylxylylene diisocyanate

MDI : 4,4'-diphenylmethane diisocyanate

PEG-600: polyethylene glycol with an average molecular weight of 600

[0018]

Table 2-a

Active Agent No.	Average molecular weight (x 10^3)	Viscosity (P at 20 °C)	Isocyanate content (%)
1	15	52	5.5
2	15	59	5.2
3	18	90	3.8
4	14	49	6.2
5	10	33	10.5
6	30	160	2.0
7	12	40	5.8
8	11	35	5.5
9	18	90	4.3

Table 2-b

Active Agent No.	Average molecular weight (x 10^3)	Viscosity (P at 20 °C)	Isocyanate content (%)
10	15	50	5.8
11	15	62	5.7
12	14	75	5.6
13	15	55	6.5
14	112	44	6.2
15	25	130	3.7
16	22	120	3.2
17	12	42	6.7

[0019]

Curing agent preparation case 1

A 1-L four-necked flask equipped with a stirrer and a condenser was charged with 130 g of 4,4'-diaminodiphenylmethane (product of Sumitomo Chemical) and 170 g of MEK and the contents were heated at 50 °C for 1 hour to make a solution. Curing agent B-1 was obtained in an amount of 295 g.

[0020]

Curing agent preparation case 2

The procedure of preparation case 1 was repeated on 130 g of 1,1-bis(4-amino-3-methylphenyl)cyclohexane (Taoka Chemical) and 170 g of MEK to give 297 g of curing agent B-2.

[0021]

The thus prepared active agent A and curing agent B were applied to a substrate and subjected to a variety of performance tests by the methods described below. The results are shown in Tables 3-a and 3-b. Experiments were also conducted but without adopting the invention; the results are shown as Comparative Examples 1~4 in Table 3-c. The parameters, pot life, cure time and abrasion wear, listed in Table 3 were measured by the following methods.

[0022]

(1) Preparing coating material and measuring the pot life

The active agent (300 g) was mixed uniformly with the curing agent in one of the proportions listed in Table 3 and 180 g of dichloromethane to prepare a coating material. When the active agent had high viscosity as in Examples 6 and 9 and in Comparative Examples 3 and 4, the amount of dichloromethane was increased from 180 g to 300 g. The thus prepared coating material was applied to a slate board about 30 cm distant by ejecting with a handy painter (Wager Model W-200). The process of ejecting was repeated until the applied coating material started to produce sticky strands and the time to that phenomenon is defined as the pot life. The test was conducted at 25 °C.

[0023]

(2) Measuring the cure time

The coating material was applied to a glass plate with a 3-mil applicator and the applied coat was cured at 25 °C x 65% r.h. until it felt hard to the touch. The time required for that phenomenon to occur is defined as the cure time.

[0024]

(3) Measuring the abrasion wear

Five films of the coating material were applied to a slate board by means of a handy painter and left to stand for 3 days at 25 °C x 65% r.h until it dried. The thus prepared test sample was set on a Taber abrader and the abrasion wear

of the sample was measured in accordance with JIS K 7204 to evaluate the wear resisting property of the sample. Test temperature, 25 °C; truck wheel, H-18; load, 500 g (one wheel); rpm, 1000.

[0025]

[Table 3-a]

Table 3-a

Example	Active agent	Curing agent	A/B mixing ratio	Pot life	Cure time	Coat's appearance	Abrasion wear	Relative rating
	A-	B-						
1	-1	-1	5/1	80	90	○	40	◎
2	-2	-1	5/1	60	73	◎	42	◎
3	-3	-1	5/1	55	70	◎	40	◎
4	-4	-1	5/0.7	65	75	○	46	○
5	-5	-1	5/2	45	55	○	42	○
6	-6	-1	5/0.4	40	80	○	48	○
7	-7	-1	5/1.1	52	70	◎	43	◎
8	-8	-1	5/1.1	55	70	◎	42	◎
9	-9	-1	5/0.8	50	80	○	47	○
10	-10	-1	5/1.1	55	70	○	42	○

Table 3-b

Example	Active agent	Curing agent	A/B mixing ratio	Pot life	Cure time	Coat's appearance	Abrasion wear	Relative rating
	A-	B-						
11	-11	-1	5/1.1	65	80	○	43	◎
12	-2	-2	5/1.5	60	72	◎	42	◎
13	-10	-2	5/1.2	50	72	○	45	○
14	-12	-1	5/1	40	70	○	47	○

Table 3-c

Comparative Example	Active agent A-	Curing agent B-	A/B mixing ratio	Pot life	Cure time	Coat's appearance	Abrasion wear	Relative rating
1	-13	-1	5/1.3	70	62	○	58	×
2	-14	-1	5/1.2	90	120	×	95	×
3	-15	-1	5/0.7	15	40	△	68	×
4	-16	-1	5/0.6	35	62	○	49	×
5	-17	-1	5/0.2	65	82	○	55	×